UNITED STATES – JAPAN
WORKSHOP ON STANDARDS FOR
EMERGING TECHNOLOGIES

Small-angle neutron scattering on AIST purified multi-walled carbon nanotubes

Vivek Prabhu

Materials Science and Engineering Division

National Institute of Standards and Technology

Toshiya Okazaki, Takeshi Eitoku, Haruhisa Kato, Masayoshi Tange

National Institute of Advanced Industrial Science and Technology

12 February 2015

Material Measurement Laboratory

Measurement science, technology, standards, models and data that support…

- Materials Science and Engineering (MSED)
- Materials Measurement Science (MMSD)
- Biosystems and Biomaterials (BBD)
- Biomolecular Measurement (BMD)
- Chemical Sciences (CSD)
- Applied Chemicals and Materials (ACMD)

Materials

MSED: design, development, manufacture, and use of materials by industry.

MMSD: next-generation characterization of materials ID, structure, composition and properties on all scales.

Bioscience

BBD: quantification of biological systems, materials and processes, from the nano to macro-scale.

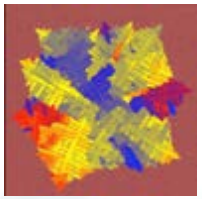
BMD: determination of the composition, structure, quantity, and function of biomolecules, including protiens, DNA, lipids and metabolites.

Chemistry

CSD: determination of chemical composition and structure of gases, organic, and inorganic species, properties and processes, reactivity and mechanisms.

ACMD: design, production, and assessment of chemical and material products, with a focus on reliability.

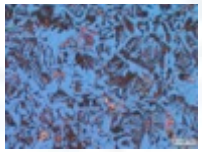
Materials Science and Engineering Division



Chief: Eric Lin

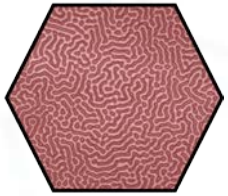
Function:

Provides the measurement science, standards, technology, and data required to support the Nation's need to design, develop, manufacture, and use materials.



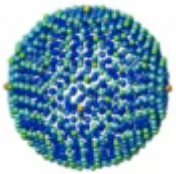
Groups:

- Polymers & Complex Fluids (Kate Beers)
- Functional Polymers (Chris Soles)
- Functional Nanostructured Materials (Albert Davydov)
- Mechanical Performance (Jon Guyer)
- Thermodynamics and Kinetics (Carrie Campbell)



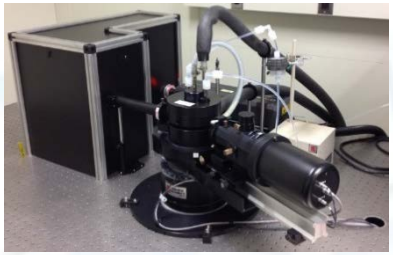
Capabilities:

- Metallurgical materials science (e.g. alloys, solidification, processing)
- Polymer & colloidal materials science (e.g. carbon nanotubes, nSoft)
- Microstructure, nanostructure (e.g. microscopy, scattering)
- Mechanical performance (NCAL, ballistic fibers)
- Materials data and computational tools (MGI)



Optical, fluorescence, and light scattering laboratory

transport properties & structure of solution-dispersed polymers, nanoparticles and gels



Static and dynamic light scattering

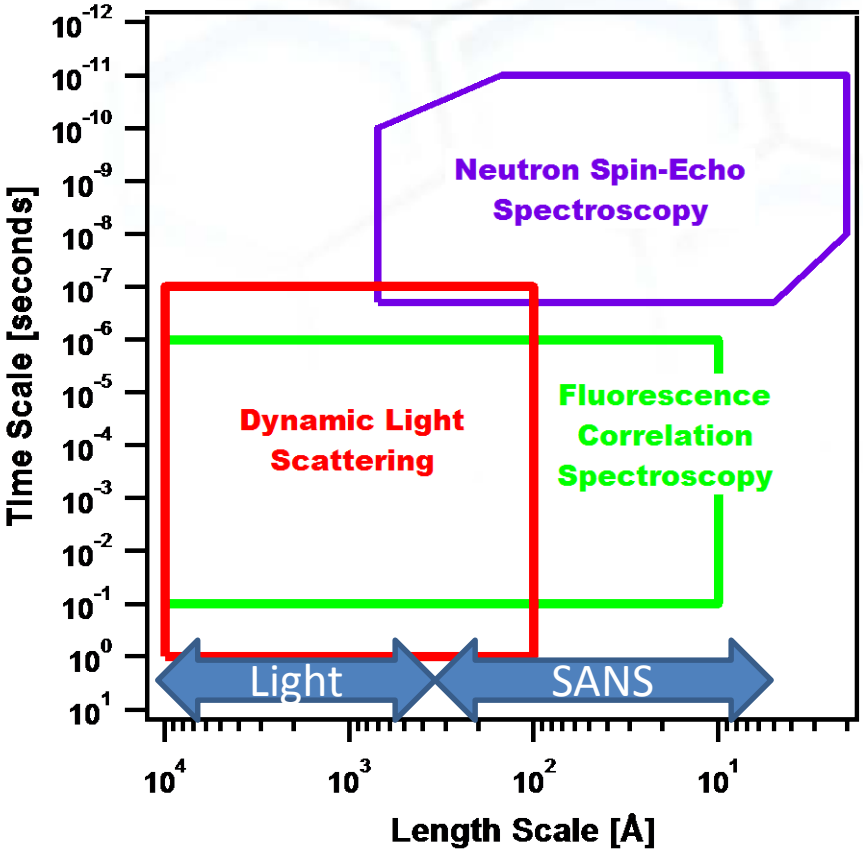
- Brookhaven Goniometer
- 532 nm polarized and depolarized

Fluorescence correlation spectroscopy

- Multi-laser line visible
- Near-nfrared detection (SWNT)
- Diffusion coeff. in multi-component

Neutron scattering

- NIST Center for Neutron Research
- Small-angle neutron scattering
- nSOFT industry consortia focus
- Novel Electrochemical SANS method



Self-assembly of biomaterials

Technical Need:

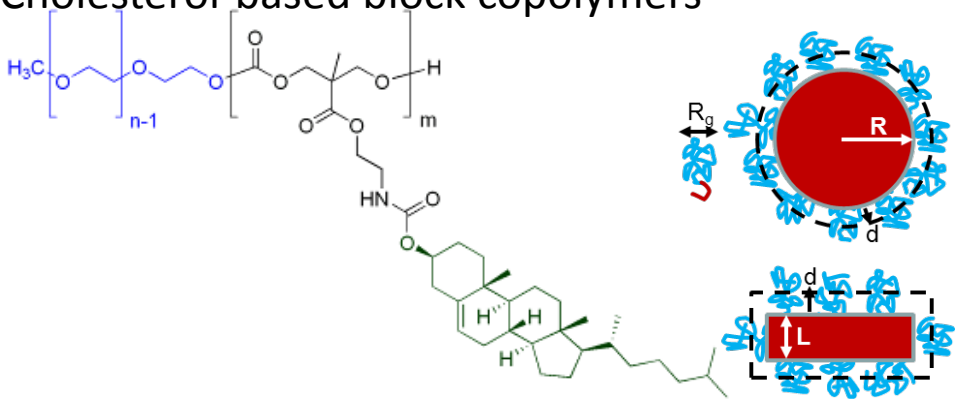
- Nano-scale carriers of well-defined size and structure to deliver a wide-variety of hydrophobic drugs with limited solubility under physiologic conditions.
- Self-assembled polymer-based nanoparticle and gel carriers are manufacturable platforms.

Structure and phase diagram characterization

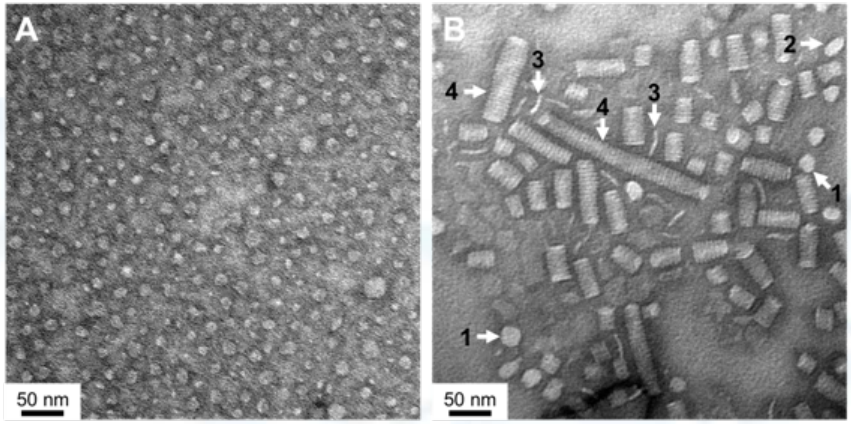
- Neutron and light scattering

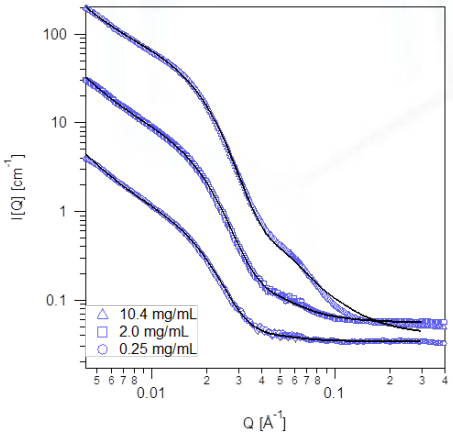
Novel Materials

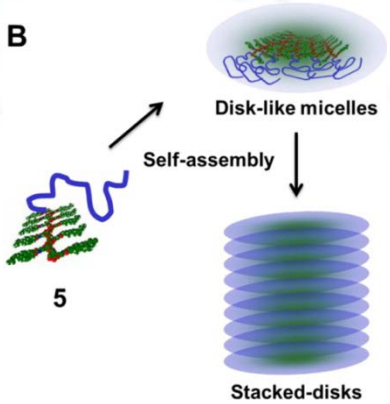
- Cholesterol-based block copolymers



S. Venkataraman et al. Macromolecules 46, 4839 (2013)







Customers and Partners

IBM

Institute of Bioengineering and Nanotechnology A*STAR

CHiMaD

NIST Materials Genome Initiative

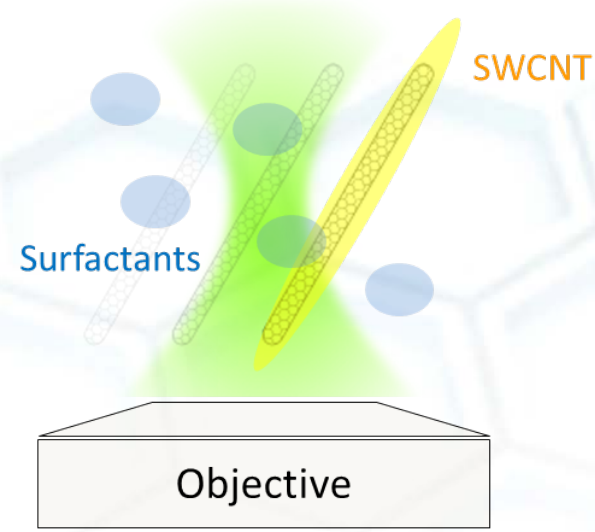
Transport properties of solution-dispersed single-walled carbon nanotubes

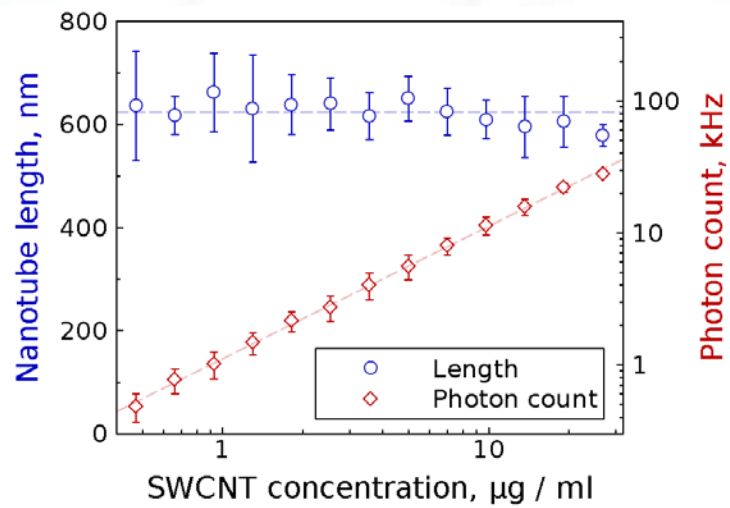
Technical Need

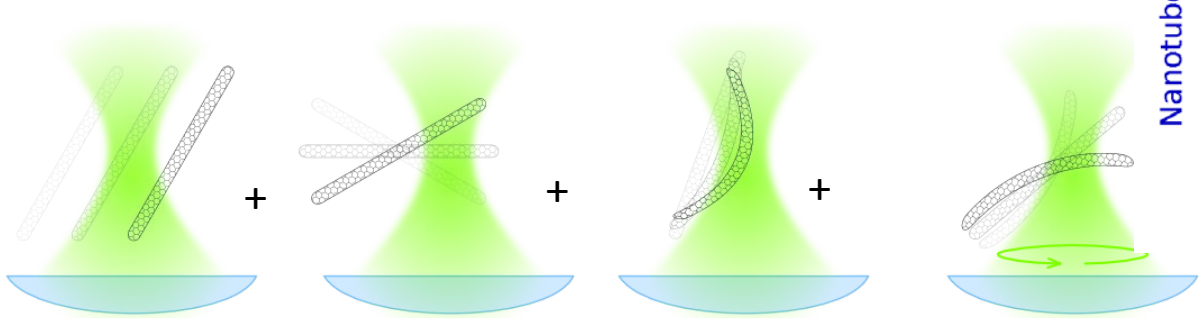
- SWNT reference materials require characterization under a variety of solution conditions, some in the presence of solubility-enhancing components that interfere with basic measurements.

Objectives

- Develop near-infrared fluorescence correlation spectroscopy (FCS) to characterize the transport properties of length-fractionated semiconducting SWNT.
- Utilize intrinsic band-gap fluorescence
- Develop basic physical characterization and highlight concentration ranges, demonstrate interactions, and limitations







Translational Rotational Bending modes Orientation

With D. Pristinski, J. Fagan

Characterization of aqueous-*dispersed* MWNT by Small-angle neutron scattering

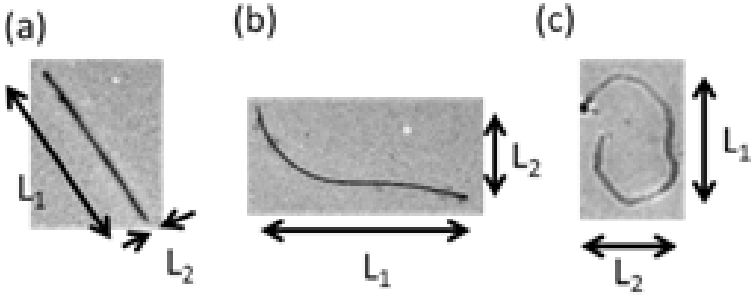
Technical Need:

- ISO TC229 Nanotechnology: Task Group on Measurement and Characterization for Environmental Health and Safety (EHS)
- Comparative measurement methods for physical and chemical properties of nanoparticles.
- NIST and AIST have complementary expertise and experience with a wide variety of nanomaterials.

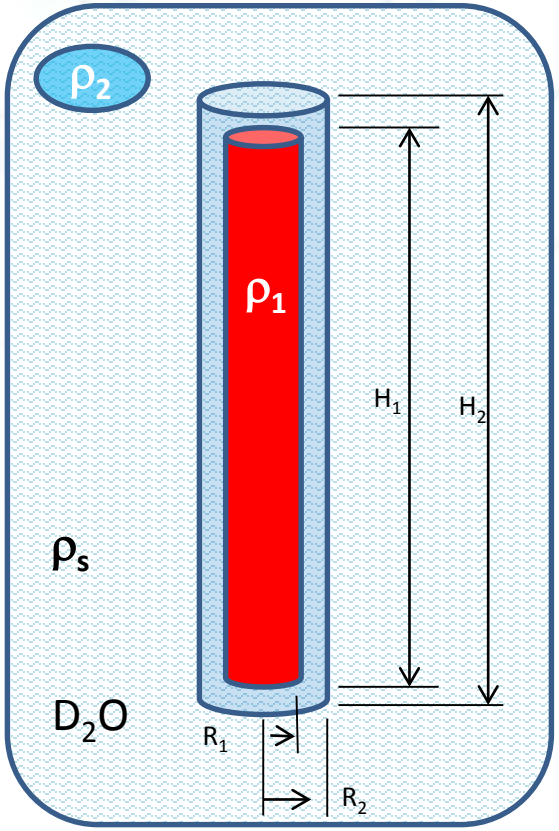
Goals:

- Initiate a collaborative study on the structure and stability of multi-walled carbon nanotubes (MWNT) in aqueous solutions by multiple methods including neutron scattering, and angular-resolved static and dynamic light scattering.
- Structure and aggregation state via SANS of surfactant-stabilized Arc-discharge and CVD- prepared MWCNT.

(a) Arc AIST(Arc-discharge) purified
(c) C-nano Co. Ltd. (CVD) as received
(b) Nikkiso Co. Ltd. (CVD) purified
(d) Hodogaya Co. Ltd. (CVD) purified



SANS Model: stiff-cylinder for MWNT/Triton dispersions



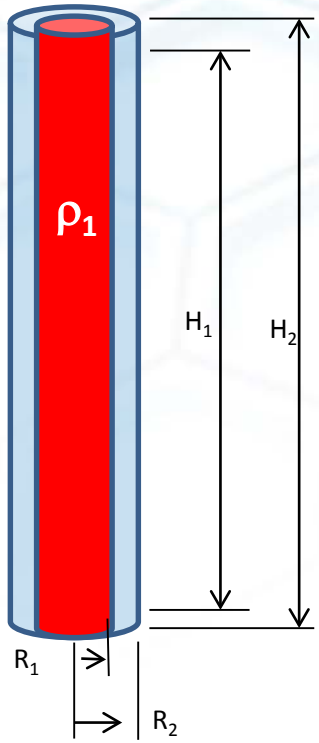
$$I(Q) = IM_{WNT}(Q) + Im_{icelle}(Q) + \text{background}$$

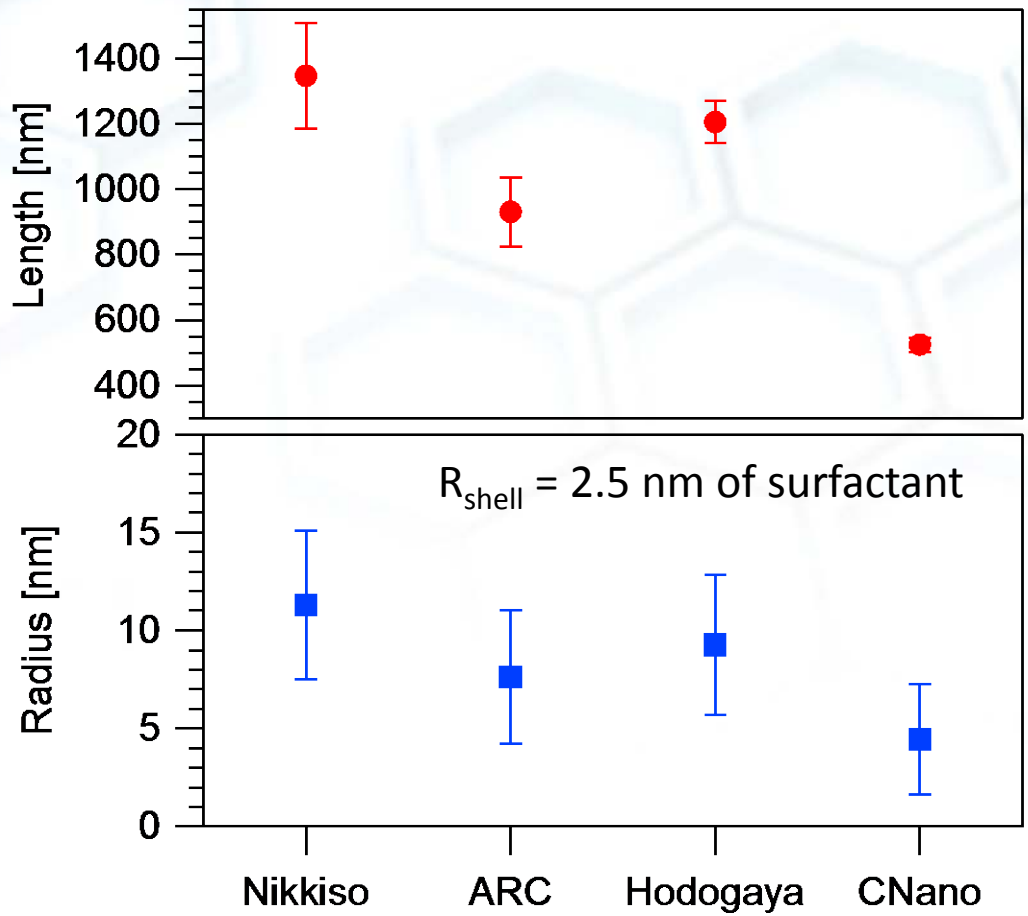
TritonX-100 coated carbon cylinder

+ Free TritonX-100R micelle

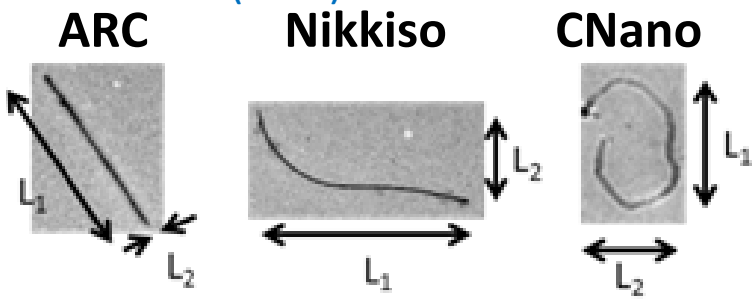
ϕ_c	= fit (volume fraction of core shell cylinder)
R_1	= fit (core radius)
σ	= fit (polydispersity of R_{core}), log-normal dist.
H_1	= fit (cylinder length), no end caps, so $H_1 = H_2$.
T_{shell}	= fixed = 25 Å (thickness of shell = micelle R_g)
	$R_2 = R_1 + T_{shell}$
ρ_1	= fixed (SLD of carbon-fullerene)
ρ_2	= fixed (SLD of micelle)
ρ_s	= fixed (SLD of D_2O)

SANS: MWNT dimensional characterization



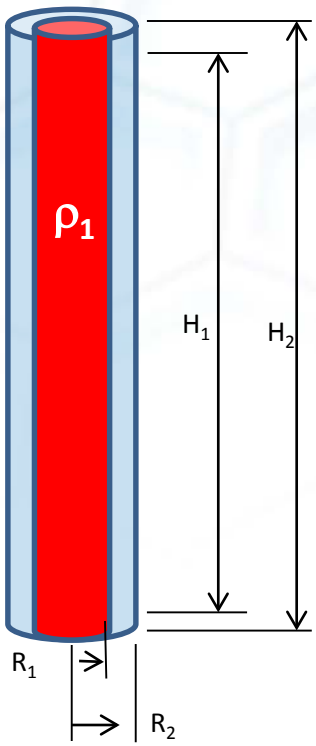


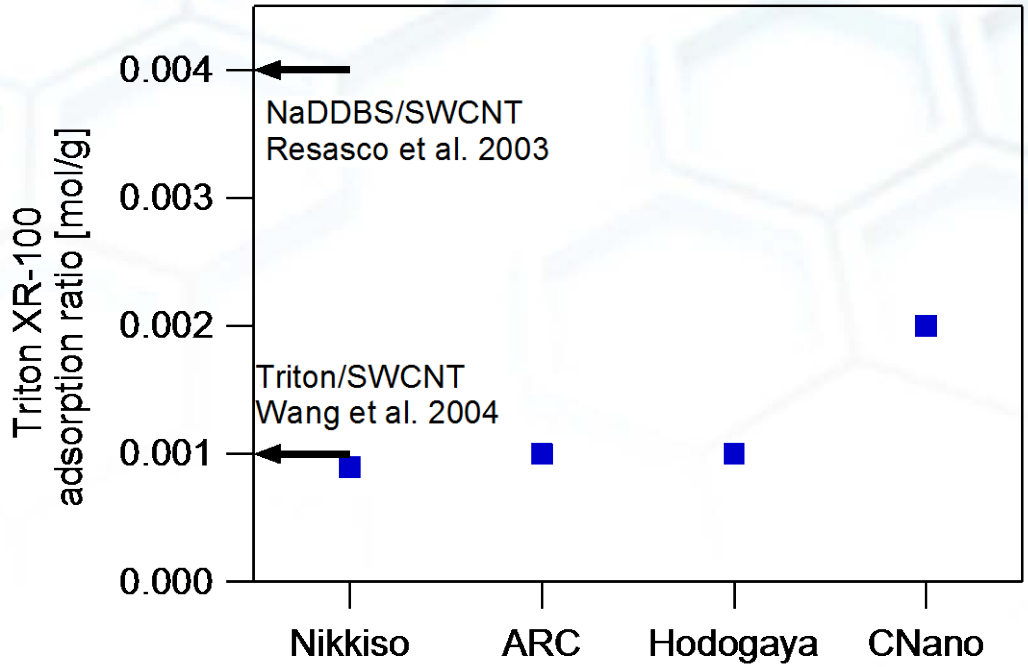
TEM Results (AIST)



Okazaki, Eitoku, Tange, Kato, and Prabhu in JSPE International Symposium

Triton surfactant adsorption onto MWNT



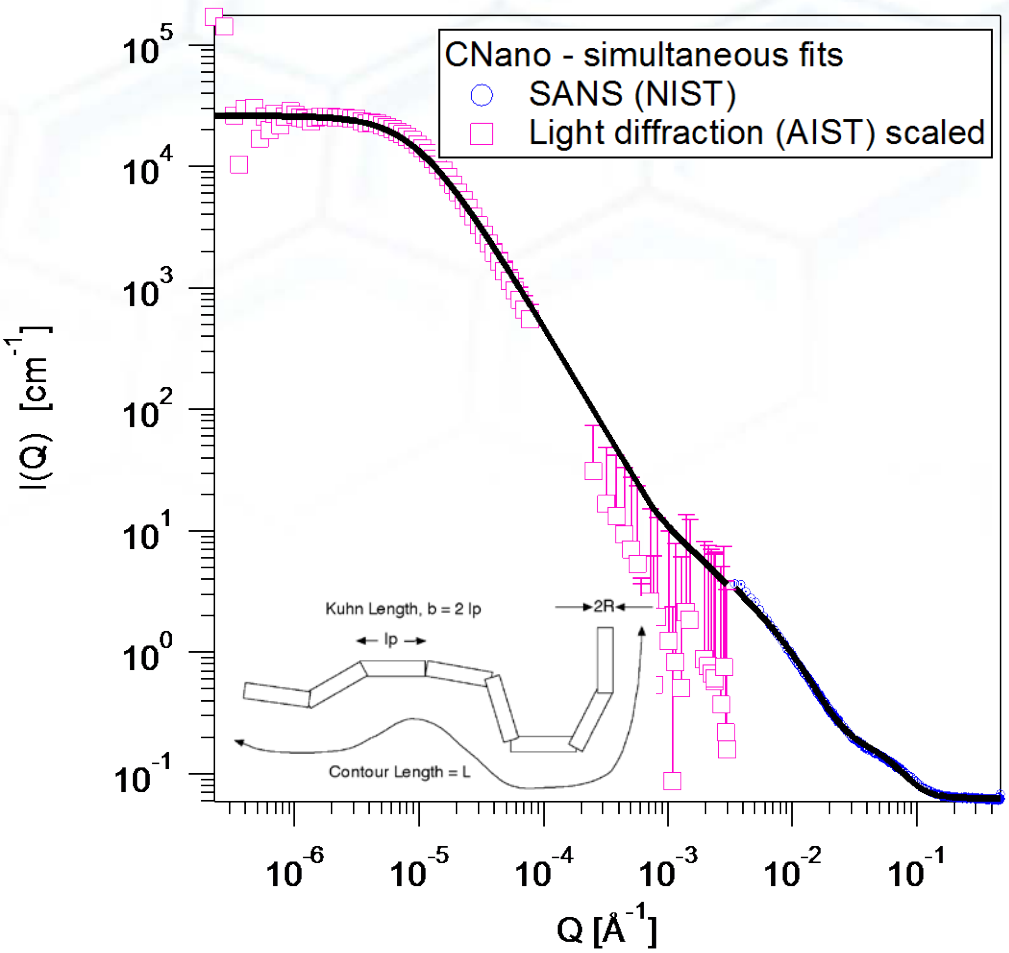


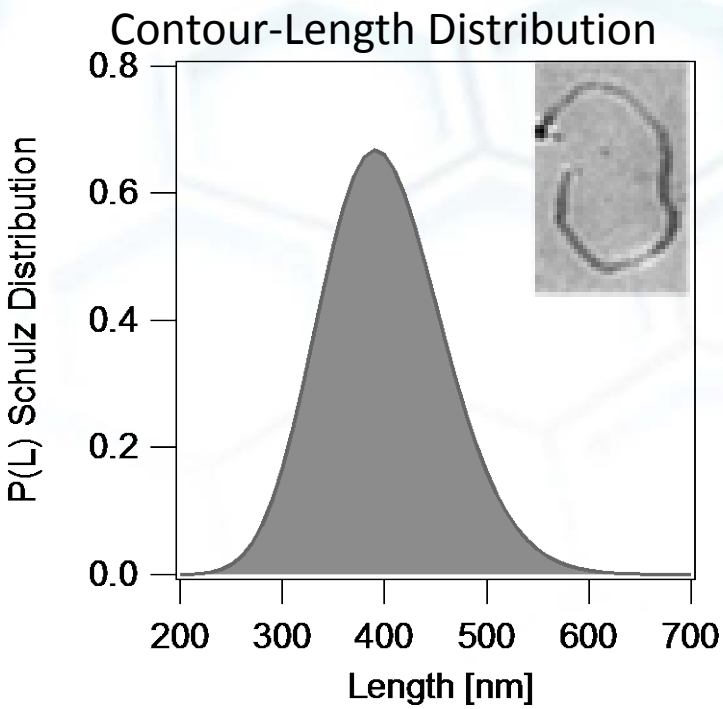
- Ratio of C_{Triton} (mol/cc) to C_{MWNT} concentration (g/cc)
- Estimates adsorption extent for monolayer coverage

- Triton XR-100 molar adsorption extent ($1.2 \pm 0.4\ 10^{-3}$ mol/g) to MWNT is comparable to SWNT

CVD Combined Light & Neutron Scattering

semi-flexible cylinder (worm-like) model





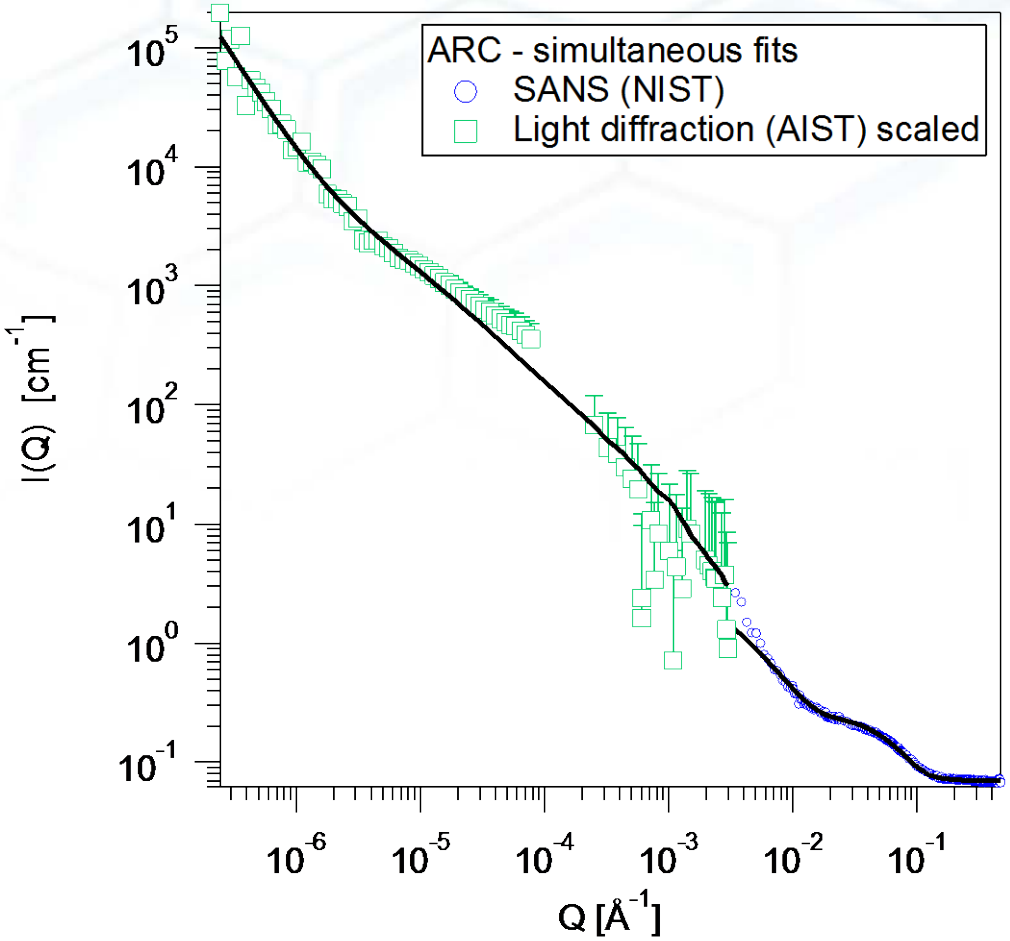
Neutron scattering

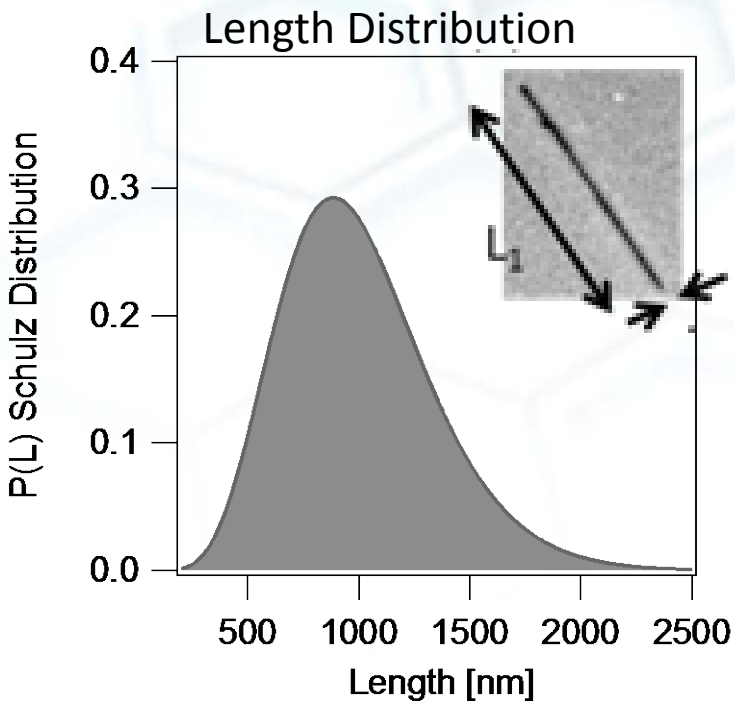
- Surfactant on MWNT
- Cross-sectional radius

Light diffraction

- <Length> = 400 nm, z = 10
- persistence length (440 ± 20 nm)

ARC: Combined Light and Neutron Scattering polydisperse cy*linder model*





Neutron scattering

- Surfactant on MWNT
- Cross-sectional radius

Light diffraction

- <Length> = 1000 nm , z = 7.4

Conclusions

Purpose: Characterization via neutron scattering of surfactant-stabilized Arc-discharge and CVD-prepared MWNT dispersions

MWNT dispersions by SANS

- ✓ Surfactant-coated cylinder with polydispersity in radius + free micelles
- ✓ Cross-sectional dimension and surfactant-MWNT properties
- ✓ Triton XR-100 molar adsorption to MWNT is comparable to SWNT
- × Not adequate for length or aggregation. Beyond resolution.

SANS + Light diffraction: simultaneous model fittings

- ✓ Light scattering/diffraction complements SANS
- ✓ CVD MWNT: semiflexible, polydisperse long thin cylinders – guided by TEM
- ✓ ARC MWNT: polydisperse long, thin cylinders– guided by TEM

On-Going Interest/Future work: MWNT cluster size by fluorescence correlation spectroscopy

New MWNT:

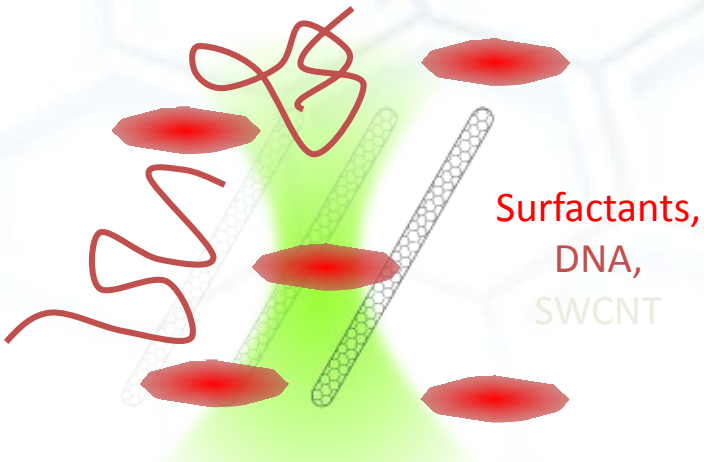
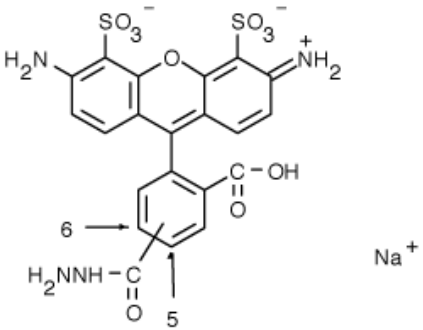
- VGCF made by SHOWA-DENKO.

Purpose:

- Comparison of disc centrifuge size distribution with fluorescence correlation spectroscopy
- Polymer-dispersed MWCNT
- Challenge -multi-component solution

Progress:

- AlexaFluor488-dye labeled Poly(ethylene glycol) stabilized VGCF MWNT procedure completed by AIST
- Samples shipped to NIST
- Measurements planned for March 2015



Alexa Fluor 488